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**Materials Science Research**

**by**

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## **INTRODUCTION**

Microgravity materials processing experiments provide an opportunity to perform scientific research in an environment which allows one to observe various phenomena without the masking effects of gravity-driven convective flows, buoyancy, or contaminating influences of walled containers. Even for the most experienced scientists, it is still difficult to predict beforehand, whether or not, microgravity experimentation can be successfully performed in space and achieve solutions to problems which are not attainable in 1 g. Consequently, experimentation in ground based facilities which are capable of simulating, in somewhat lesser time frames and to a lesser degree of microgravity, provides a unique low-cost approach to determine the feasibility of continuing research in a particular experiment. The utilization of these facilities in developing the full requirements for a space experiment does present a very cost-effective approach to microgravity experimentation. The Drop Tube Facility at Marshall Space Flight Center (MSFC) provides an excellent test bed for containerless processing experiments such as described here. These facilities have demonstrated for a number of years the capability to develop insight into space experiments involving containerless processing, rapid solidification, and wetting phenomena through the use of lower-cost ground facilities. Once sufficient data has been obtained, then a space-based experiment can be better defined.

Containerless processing of materials provides an excellent opportunity to study nucleation phenomena and produce unique materials, primarily through the formation of metastable phases and deep undercooling achieved through falling drops of molten material. Extended solute solubilities and greatly refined microstructure can also be obtained in containerless processing experiments. The Drop Tube Facility at Marshall Space Flight Center has been an integral part of that area of research. The University of Alabama in Huntsville has been fortunate to have participated in designing new

experimental systems and performing a large number of the research experiments carried out at the MSFC Drop Tube and Drop Tower Facilities.

Since drop tube experiments provide a containerless free fall for about 4 seconds and consequently also simulate microgravity (performed in a vacuum), the materials of most interest to study are immiscible systems, monotectics and eutectics. The current facility capability to monitor droplet temperatures above 1500° C dictates the types of systems applicable to this proposal. However, improving the capability of the remote temperature measurement down to 1000° C will increase the range of experiments possible. As mentioned above, containerless processing experiments carried out in space are much more expensive than those performed at the ground-based facilities. Therefore the preliminary experiments performed in the ground-based facilities at MSFC are extremely useful in preparation for developing the necessary information to propose a space-based experiment.

## **EXPERIMENTAL**

The first task of this project was to find a high temperature (HT) immiscible binary system that has (1) a monotectic temperature above 1000° C, (2) a low vapor pressure, (3) a wide miscibility gap, (4) low oxygen affinity, (5) available thermophysical properties, and (6) a reasonably accepted phase diagram. Data on these six items were obtained from NIST and other sources and were combined into an interactive database. Most of the items were found to be mutually exclusive from each other: HT immiscibles having high consolute temperatures do not have low vapor pressures; the HT immiscibles that did have low vapor pressures had very high oxygen affinities (i.e., rare earth elements); experimentally determined phase diagrams were not readily available - only theoretically calculated diagrams. Of the systems attempted in this study, only one has shown to be promising.

Initial studies used the Sn-Cr and the Ag-Ni systems. Both were arc-melted in bulk form to make the starting materials. Electromagnetic levitation was used as the processing technique in the Drop Tube Facility. Processing these alloys was not successful. Upon melting, they immediately began to vaporize creating a plume which coated and blocked the pyrometer viewport, or arced the levitation coil if processed in a vacuum. Additionally, the sample did not remain stable within the coil as it was being heated through the liquid-liquid region of the miscibility dome: the samples either sheared themselves apart from uncontrolled spinning or fell out of the coil with a large horizontal velocity component which made them hit the Tube walls. In an attempt to reduce the vaporization problem, two modifications were made: using a Ti-Ce system and pressed powder Ag-Ni pellets.

Cerium is a rare earth metal with an equilibrium oxygen partial pressure of less than  $10^{-30}$  atmospheres at  $1000^{\circ}$  K and even less at room temperature. Conversations with the Rare-Earth Information Center also suggested that just a small addition of oxygen (~500 ppm) into the binary system could eliminate the immiscibility of the phase diagram. The Ti-Ce droplet starting material was created using the same techniques as with the previous systems. Great care was taken to use a glovebox and to keep the Cerium and alloys under ethanol to prevent oxidation. These alloys did perform much better in the levitation coil with regards to evaporation. However, oxidation on the surface of the droplets, both before, during, and after dropping could not be prevented.

Recalescence due to undercooling was seen on two of the Ti-Ce drops. However, the problem of oxidation could not be eliminated as the source of nucleation as opposed to the wetting effect attempted to be observed in this study. The use of a hydrogen atmosphere to lessen the oxygen problem was investigated but was found to be not as effective a getter as the cerium was an oxidizer. The Ag-Ni powdered pellets were attempted next.

The use of powders as initial starting materials was proposed as a means of approaching an ideal mechanical mixture which when sintered would allow the elements to be more closely in a solid state solution. This would then reduce the activity of the more vaporous

element and allow the processing of the pellet with much less vaporization. The powder pellet production technique used 99.9% purity 2 $\mu$ m diameter Ni and 0.75 $\mu$ m diameter Ag. Samples were pressed into roughly 0.5 cm diameter x 0.4 cm height pellets at a pressure of 145 kpsi. Samples were reduced in a flowing pure hydrogen atmosphere at about 300C for 4 hours. Sintering was then performed at 1000C (70% of the monotectic temperature) for 100 minutes with a flowing He-5%H environment.

## RESULTS

Processing of the resulting powder pellets in the Drop Tube produced the same vaporization problem as the bulk Ag-Ni materials. This continuing vaporization problem should be understandable from the fact that the interaction energy between two elemental atoms in an immiscible solution is positive and thus are not attracted to each other. Thus the lower vapor pressure atom sitting on the surface of an immiscible liquid will not be kept from evaporating by any neighboring atoms. Referring to Table 1a, two systems, Cu-V and Ga-V, were attempted due to the low vapor pressure of the individual constituents. The Au-Ru would not be the more acceptable alloy because Ru is only available in powder form and the cost of Au and Ru is prohibitive (~\$10k for 60 drops).

The vanadium used for this study was initially 99.93% pure, but was so old that a black oxide layer had formed on the chips. Before it could be used, the chips were ultrasonically cleaned in a 20%HF, 20% nitric, water balance solution for 15 minutes. The 99.9% copper was similarly cleaned. The Cu-V alloys (Figure 1) were arc-melted into starting materials just as the previous alloy systems. When processed in the levitation coil under vacuum, vapor coating of the pyrometer optics became noticeable. However, the coil did not arc. Samples were very unstable upon melting and were constantly hitting the coil and sticking, or hitting the side of the Tube upon release. More coil experimenting may solve these problems.

The Ga-V alloys (Figure 2) were kept frozen until arc-melted. As the phase-diagram shows, since the Ga-rich phase is the majority phase, the alloy tended to liquefy as its

temperature rose to room temperature. Because the gas through which the sample must drop in the Tube is at room temperature as well as the plate upon which it impacts, most of the drops made in the Tube did not have time within the 4.6 seconds of drop time to reactively form all of its phases and thus were still semi-liquid upon retrieval. Vapor plumbing was a minor problem, but the fact that the samples were not completely solid upon retrieval made the achievement of the second objective of this study impossible: analysis of the interior minority phase droplet distribution.

## **SUMMARY**

The most promising system for DROP TUBE research appears to be the Cu-V system. Levitation coils and processing conditions will be varied to attain stable levitation and good pyrometry. The stable overheating of liquid metals is a major problem for all DROP TUBE levitation experiments but especially the high consolute temperature immiscibles. If stable levitation can be accomplished, then quantifiable undercooling can be observed if it occurs.

Powder pressed immiscible samples are not any less vaporous than bulk starting materials when taken into the liquid state. Noble metals may be worth attempting because of their lack of oxygen affinity; however, they are very cost prohibitive and may still have a vapor problem.

The objectives of this research can possibly be reached in a less-arduous manner by performing low-temperature experiments in other facilities. Lower temperature immiscible systems can be found which satisfy all 6 criteria stated in the opening paragraph. If optical pyrometry is available for these lower temperature ranges, these experiments could be performed in most levitation devices (one-g) and on the parabolic airplane flights (low-g). However, the longer cooling times for lower temperatures may rule out the use of anything but long-duration microgravity capabilities.

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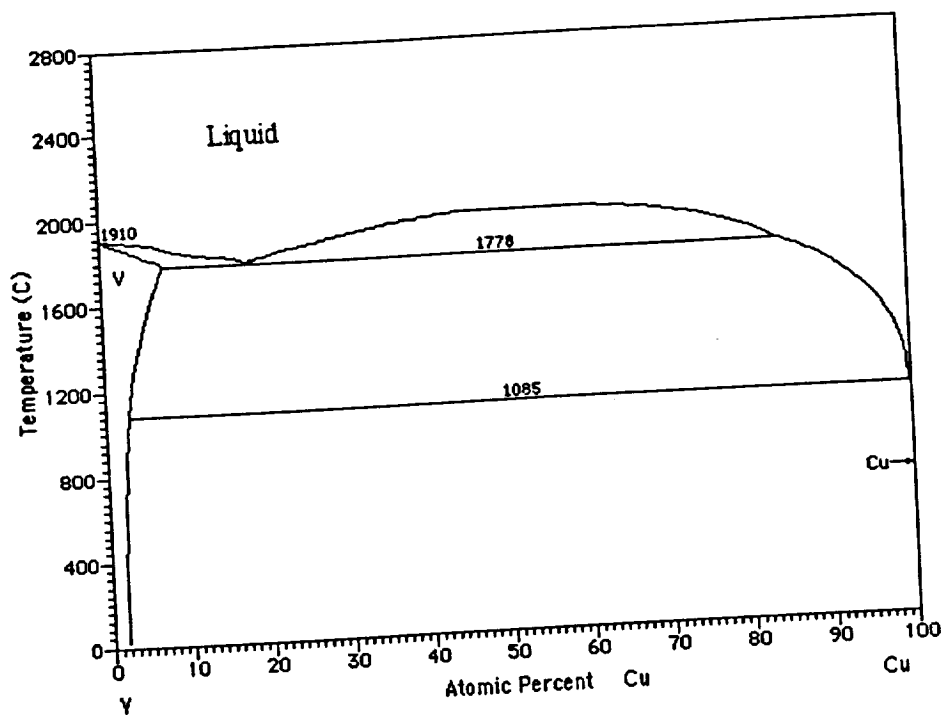
Table 1a. Monotectic ( $T_m$ ) and consolute ( $T_c$ ) temperatures, immiscibility gap ranges, consolute compositions, and constituent vapor pressures ( $V_p$ ) of alloys whose  $T_m > 1000\text{C}$  and whose  $V_p < 1$  Torr at  $T_m$ . The Lanthanides and Actinides were not considered due to toxicity or  $\text{O}_2$  affinity. A value of 1000 for gap ranges or 0 for T means N/A.

Binary Alloy	Mono T (C)	Cons T (C)	Gap Range (a/o of 2nd ele)		Cons Comp	Vapor P at Tmono (Torr)	
						ele#1	ele#2
Cu- V	1530	2580	4.0	86.4	50.0	4.23E-01	8.70E-05
Ag-Mn	1185	0	50.3	96.6	1000.0	1.41E-01	5.34E-01
Au-Ru	1066	2190	1000.0	1000.0	50.0	1.79E-05	8.22E-12
Ga- V	1080	1210	9.0	35.0	22.5	1.54E-02	2.12E-09

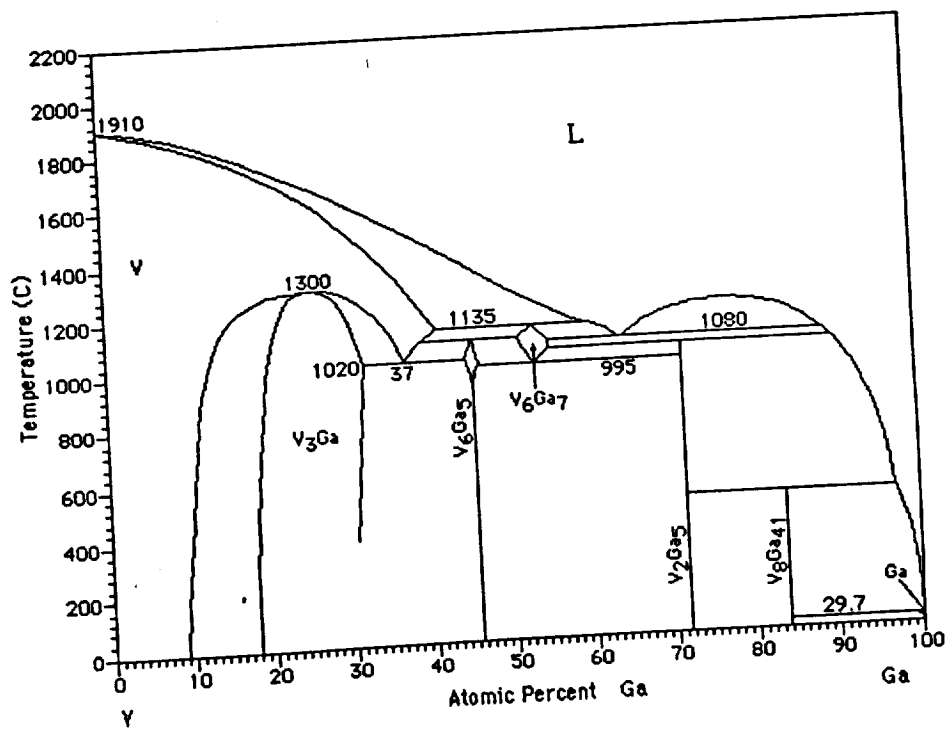
Table 1b. Same as Table 1a except the constituent vapor pressures ( $V_p$ ) are evaluated at  $T_c$ .

Binary Alloy	Mono T (C)	Cons T (C)	Gap Range (a/o of 2nd ele)		Cons Comp	Vapor P at Tmono (Torr)	
						ele#1	ele#2
1 Au-Rh	1885	2509	17.5	70.0	57.2	1.72E+02	1.13E+00
4 Nb-Mg	2380	0	1000.0	1000.0	1000.0	5.20E-136	5.23E-19
7 Nb-Cu	1550	0	70.0	85.0	1000.0	5.20E-136	4.40E-52
8 Cu- V	1530	2580	4.0	86.4	50.0	9.48E+02	1.11E+01
9 V-Mg	1860	0	0.0	100.0	1000.0	1.81E-82	5.23E-19
13 Ag-Cr	1445	0	15.0	96.5	1000.0	1.05E-42	1.63E-62
14 Ag-Mn	1185	0	50.3	96.6	1000.0	1.05E-42	5.40E-42
15 Ag-Ni	1435	0	2.0	95.0	1000.0	1.05E-42	3.45E-67
17 Bi-Co	1345	0	2.0	82.0	1000.0	1.63E-29	1.11E-66
18 Bi-Mn	1240	0	1.0	46.0	1000.0	1.63E-29	5.40E-42
21 Pb-Co	1492	0	2.0	100.0	1000.0	1.91E-28	1.11E-66
22 Cu-Cr	1470	0	42.0	94.0	1000.0	4.40E-52	1.63E-62
24 Sn-Cr	1440	0	0.0	95.0	1000.0	1.05E-48	1.63E-62
26 Pb-Fe	1530	0	0.0	100.0	1000.0	1.91E-28	3.78E-63
30 Pb-Mn	1198	0	26.4	98.0	1000.0	1.91E-28	5.40E-42
31 Sr-Mn	1240	0	3.5	99.2	1000.0	3.12E-24	5.40E-42
32 Tl-Mn	1198	0	95.0	0.0	1000.0	1.15E-25	5.40E-42
33 Pb-Ni	1340	1554	88.0	43.7	29.9	3.04E+02	1.52E-02
34 Pb-Si	1397	2047	3.0	97.0	1000.0	4.08E+03	7.42E-01
44 Au-Ru	1066	2190	1000.0	1000.0	50.0	2.49E+01	1.83E+00
45 Ba-Ni	1325	1485	1000.0	1000.0	26.5	1.76E+02	5.45E-03
46 Bi-Cr	1553	2134	5.0	91.0	50.0	5.87E+03	1.33E+05
47 Pb-Cr	1470	2087	1000.0	1000.0	50.0	4.80E+03	9.00E+04
48 Sn-Cr	1374	1485	1000.0	1000.0	60.5	2.65E-01	9.18E+01
56 Pb-Ni	1340	1554	1000.0	1000.0	70.1	3.04E+02	1.52E-02
57 Ga- V	1080	1210	9.0	35.0	22.5	1.21E-01	8.85E-08
69 Te-Zn	1215	1340	1000.0	1000.0	82.2	7.60E+02	2.30E+04
71 Ag-Co	1489	0	1000.0	1000.0	1000.0	1.05E-42	1.11E-66
72 Ag-Rh	1900	0	1000.0	1000.0	1000.0	1.05E-42	4.09E-89





V-Cu Phase Diagram



V-Ga Phase Diagram

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16. Abstract  Containerless processing experiments in space and in ground-based facilities such as the Drop Tube Facility at Marshall Space Flight Center provide a unique capability to study materials processing phenomena without the influence of walls on nucleation processes. This research will further develop that capability by new experiments with immesible systems. Nucleation and under-cooling phenomena will be monitored using infra-red temperature measurements, with emphasis on developing FTIR capability to improve upon current methodology using commercial optical pyrometers.					
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